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RELATION BETWEEN THE PHASE COMPOSITION AND DURABILITY OF CERAMIC BRICK OLDER THAN 600 YR AT THE IPAT'EVSKII MONASTERY

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Research has shown that the brick in the Ipat'evskii monastery was made using clay with high content of quartz SiO_2 = 65 – 72%, calcium oxide CaO = 10 – 15% and Fe_2O_3 = 8 – 12%. Owing to the crystallization of mullite in the samples studied the bricks have high durability. Wollastonite, which was formed due to the elevated CaO content in the clay, creates a dense framework that impedes any change in the previous volume, i.e., it noticeably decreases stress and shrinkage in the ceramic samples.

Key words: phase composition, durability, Ipat'evskii monastery, brick, crystallization, mullite, cristobalite, hematite, wollastonite.

The problems of the durability of structures and buildings and lowering the cost of capital repairs are very topical because of the scales of commercial, housing and individual residential construction.

In the production of ceramic materials special importance is attached to the phase composition, since the phase composition and texture are the main determinants of performance [1, 2].

Economic efficiency requires that building materials have high durability, which secures building life in excess of 100 yr [2].

It should be noted that the quality of the brick manufactured in Rus' was very high since olden times. Visiting Moscow in the 16th century Petr Alenskii wrote that in this country bricks were excellent and Moscovites were very skilled brick makers [3].

The complexities and difficulties at the present stage of the historical evolution of the domestic ceramic materials industry must be attributed not only to new problems but also a break in the "ties of the times" – a sharp dissociation of the science of the last century from the study and analysis of historical experience [3]. Understanding the ties "past – present, future" makes it possible to bridge the gap between the production of ceramic materials in the past and the directions of development in the era of globalization of the post-industrial information society of the 21st century [2].

Modern methods of chemical analysis make it possible to determine the phase compositions of a ceramic material of any age.

The Ipat'evskii monastery (Fig. 1) was first mentioned in the chronicles of 1432, but it was built much earlier (in the 1330s).

The monastery (Fig. 1*a*) lies near the city of Kostroma, on the old Yaroslavl' road, which once passed along the left bank of the Volga River. Apparently, the Ipat'evskii monastery was built in the period when Kostroma rose as a distinct principality in the third quarter of the 13th century. In the 14th and beginning of the 15th centuries Kostroma became a stronghold of princely power. The monastery is first mentioned in the chronicles in a description of an internecine struggle for the throne between Galich–Zvenigorod princes in the second quarter of the 15th century.

The research was conducted using the following:

– x-ray phase analysis using a DRON-6 diffractometer and CoK_α radiation;

– FEI Quanta Inspect S electron microscope with an EDAX Genesis attachment and ultrathin window as well an ÉMB-100BR electron microscope;

– method of replicas in transmission;

– determination of elemental chemical and phase composition of brick more than 600 yr old.

The location from which a brick was taken from the Ipat'evskii monastery and the brick chosen are shown in Fig. 1*b* and *c*.

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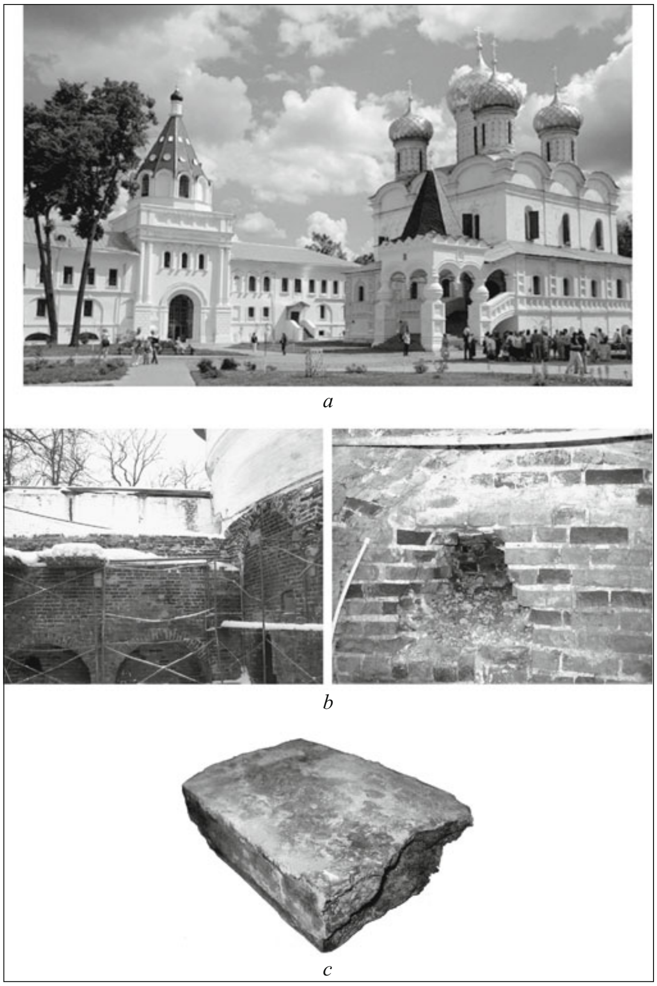

Fig. 1. Ipat'evskii monastery (*a*) and masonry samples from its walls: *b*) part of the restored wall (on the left-hand side) and location from which the brick was taken (right-hand side); *c*) 70 mm high, 180 mm wide and 300 mm long brick from the Ipat'evskii monastery.

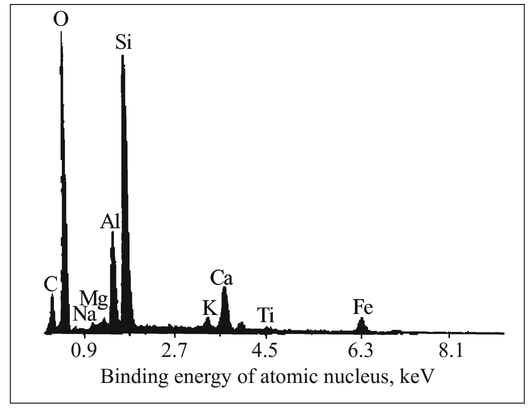

Fig. 2. X-ray spectral microanalysis of a ceramic sample from a wall of the Ipat'evskii monastery.

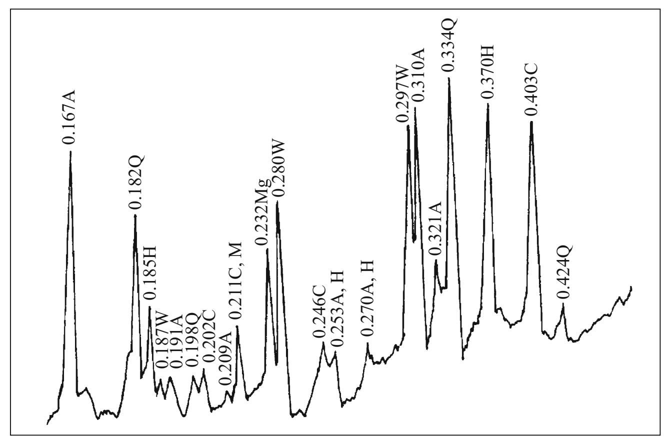

Fig. 3. X-ray diffraction pattern of brick from the Ipat'evskii monastery: A) anortite; W) wollastonite; H) hematite; Q) quartz; C) cristobalite; M) mullite; Mn) magnetite.

Elemental analysis showed that the main chemical elements of the samples are Si, Fe, Ca, C and Al (Fig. 2). The ceramic sample collected from the monastery wall includes the following elements (content, %):[2] 6.10 C, 44.86 O, 0.56 Na, 1.40 Mg, 8.48 Al, 22.11 Si, 2.42 K, 6.77 Ca, 0.74 Ti and 6.05 Fe.

Iron oxide is present in clays, mainly as an impurity, and imparts to clay a predominately reddish color after firing but light to dark burgundy for Fe_2O_3 5% [3].

High carbon content (C = 6.10%) in ceramic brick shows that consumable additives were introduced into the batch. The consumable additives are introduced into batch to 3 vol.%, i.e., 60 – 80% of the total fuel required for firing articles [3]. Iron oxides lower the melting temperature of clay appreciably only during firing in a reducing medium, and a reducing medium is created by introducing fuel into the composition of the brick.

In [4] it was shown that elevated iron oxide promotes mullite crystallization at the early stages of firing (1000 – 1050°C).

The main properties of ceramic materials are due to mullite and freeze-, acid- and heat-resistance and their strength depends on how it is formed and its structure and amount during firing [5 – 7].

Elevated calcium in the experimental samples will promote the formation of anortite and wollastonite [1].

The x-ray phase composition of the bricks studied was determined with a DRON-6 diffractometer using CoK_α radiation with the rotation rate of the sample table equal to 1 °/min.

The x-ray diffraction pattern of a brick from the Ipat'evskii monastery is displayed in Fig. 3.

In the powder diffraction pattern the strong characteristic lines at $d/n = 0.182$, 0.198, 334 and 0.424 nm are due to

[2] Here and below, content by weight, %, unless otherwise stipulated.

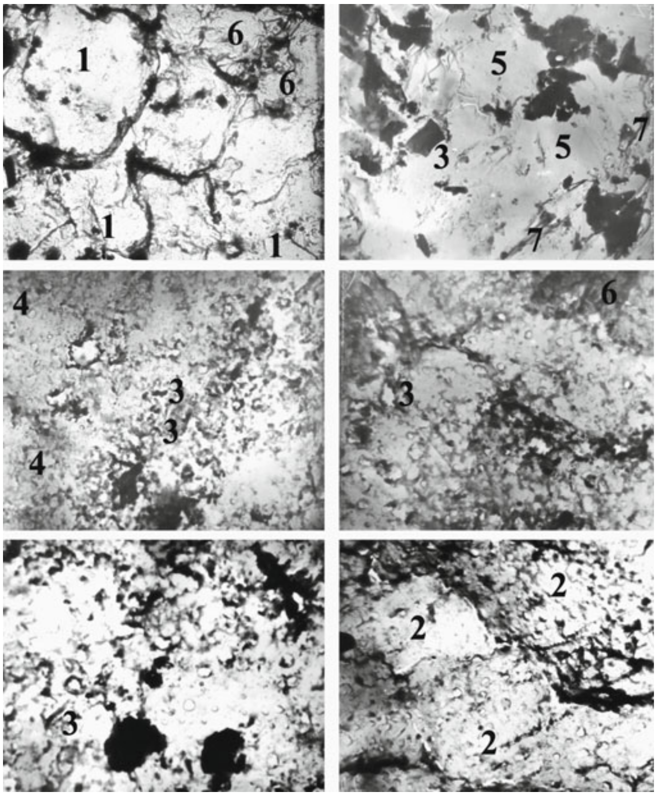

Fig. 4. Electron-microscope photographs of brick from the Ipat'evskii monastery (×500): *1*) cristobalite; *2*) quartz with fusion edge; *3*) anortite elongate-prismatic shape; *4*) primary (scaly) mullite; *5*) glass phase; *6*) hematite; *7*) wollastonite.

quartz, $d/n = 0.187$, 0.280 and 0.297 nm to wollastonite, $d/n = 0.21$ and 0.270 nm to mullite, $d/n = 0.167$, 0.191, 0.209, 0.253, 0.270, 0.31 and 0.321 nm to anortite, $d/n = 0.185$, 0.253 and 0.37 nm to hematite, $d/n = 0.202$, 0.211, 0.246 and 0.403 nm to cristobalite and $d/n = 0.232$ nm to magnetite.

As Fig. 3 shows, new minerals are formed in ceramic brick from the Ipat'evskii monastery after firing: anortite, wollastonite, cristobalite, hematite, mullite and magnetite. This attests to elevated content in the clays used of quartz $SiO_2 = 65 – 72\%$, calcium oxide $CaO = 10 – 15\%$ and $Fe_2O_3 = 8 – 12\%$. The crystallization of mullite in the sample shows that the firing temperature of the brick was at least 1050°C.

Wollastonite — calcium metasilicate β-$CaO \cdot SiO_2$ — is polymorphic. It crystallizes in two modifications: high-temperature α-modification (pseudo-wollastonite) and low-temperature β-modification (wollastonite proper). Wollastonite creates a dense framework, which impedes any change in the previous volume, i.e., appreciably lowers stress and shrinkage of ceramic articles. Wollastonite is extremely interesting, but, unfortunately, it has not been adequately studied so far [1].

The needle structure of wollastonite promotes its use in ceramic materials for reducing shrinkage. Ceramic batch with added wollastonite possesses unusual properties [1]. On heating to the maximum firing temperature this batch melts only partially, and the unmelted wollastonite, whose crystals are needle shaped, creates a dense framework impeding a change in the volume of an article. A small loss of volume is due to melting of the binding clay, which a component of the batch (during firing wollastonite practically does not change volume).

Anortite — feldspar ($CaO \cdot Al_2O_3 \cdot 2SiO_2$) — possesses all properties characteristic of feldspar mineral [1]. This alumino-silicate is polymorphous and, aside from anortite, two other unstable modifications are known. In nonmetallic materials it is encountered only in the stable modification; the melting temperature is 1550°C. There are relatively few works on the formation of crystalline embryos of anortite and its effect on the growth of strength during firing of ceramic tiles.

Anortite forms in alumina melts in the presence of calcium oxide and silicon oxide [1]:

$$CaO + Al_2O_3 + SiO_2 \rightarrow CaO \cdot Al_2O_3 \cdot SiO_2.$$

A continuous series of solid solutions called plagioclases forms with albite $NaSi_3AlO_8$ [1].

In [1] it is proposed that anortite is responsible for the growth of strength in ceramic materials.

To obtain the most complete information on structure formation in the brick from Ipat'evskii monastery the microstructure was studied with an ÉMB-100BR electron microscope by the replica in transmission method (Fig. 4).

As one can see from Fig. 4, the following phases are observed in the brick from the Ipat'evskii monastery: quartz with a fusion edge, pseudomorphoses of glass with sort-prismatic mullite; cristobalite forms plate-shaped crystals up to 5 μm in size, usually located in sections of a glass phase where there is no anortite, forming outgrowths in one or several levels.

The mullite in the brick from the Ipat'evskii monastery is represented in the form of numerous submicroscopic and short-prismatic crystals, which are located inside grains of clayey binder, cementing all components.

CONCLUSIONS

In summary, these investigations have shown that the brick used in the Ipat'evskii monastery was made using clay with elevated quartz content $SiO_2 = 65 – 72\%$, calcium oxide $CaO = 10 – 15\%$ and $Fe_2O_3 = 8 – 12\%$. Owing to crystallization of mullite in the samples the brick has enhanced durability. Wollastonite, formed as a result of the elevated content of CaO in the clay, creates a dense framework that impedes any change of the previous volume, i.e., it decreases stress and shrinkage of ceramic articles appreciably.

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